SCIENCE FOR GLASS PRODUCTION

UDC 666.1.053.511(047)

FROSTING AS A CONTEMPORARY METHOD OF GLASS DECORATION (A REVIEW)

N. I. Min'ko,[1] V. S. Bessmertnyi,[1] V. A. Panasenko,[1] S. V. Semenenko,[1] S. N. Zubenko,[1] and N. I. Voloshko[1]

Translated from Steklo i Keramika, No. 6, pp. 3 – 5, June, 2003.

Contemporary methods for frosting glass and glass articles are analyzed. The results of studies of frosting household glassware by plasma spraying of copper are described.

Frosting of household glass articles is a widespread method for decorating household, fashion, and container glass.

Standard GOST 24315–80 distinguishes seven main types of glass articles decorated in a cold state:

– articles with flat facets;
– articles with diamond facets;
– articles with dull polish;
– article treated by sandblasting;
– engraved articles;
– etched articles;
– articles decorated by hand painting, sink-screen printing, spraying, decalcomania.

At present several modern methods for dull finish of glass have been developed, which are not included in GOST 24315–80. Therefore, we will consider both traditional and nontraditional frosting methods.

We proposed a classification of all methods for dull finishing depending on the treatment technique. Such a classification is more convenient than the current one and includes five groups:

– frosting by mechanical treatment;
– frosting by chemical treatment;
– deposition of dull fired coatings
– deposition of nonfired dull coatings
– frosting by alternative energy sources.

Let us consider in more detail each group. Mechanical treatment methods include polishing, cutting, engraving, and sandblasting (shot-blasting). Let us give a brief characteristic to each method.

Grinding is removing a glass layer with an abrasive instrument. Grinding usually includes two stages. The first stage is called stripping or rough grinding using coarse-grained abrasives. In the second stage the surface is consecutively treated by finer and finer abrasive powders [1 – 4].

Cutting is a method of treatment of glass articles, in which the cutting edge of an abrasive instrument is used to create patterns in the form of various notches on the glass surface.

Engraving is a method when various images, ornaments, and inscriptions are carved on the surface [1]. Engraved patterns can be embossed or indented [2].

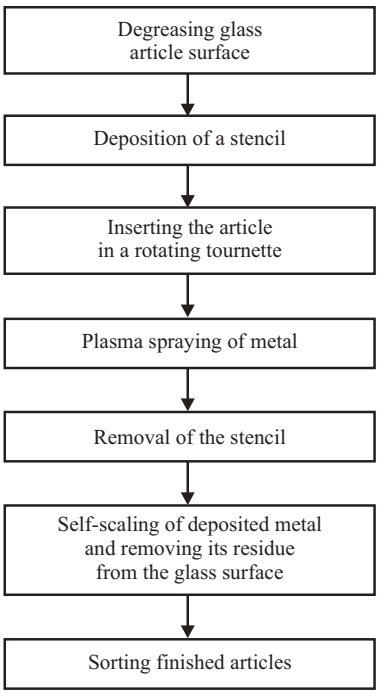
The sandblasting method implies removal of a glass layer by a jet of free abrasive material. Injection, gradient, and vacuum pneumatic plants are usually used in industrial conditions [2, 3]. Sandblasting methods are upgraded. For instance, in Ireland glass is treated with abrasive material with a prescribed granulometric composition to improve the quality of frosting.

We suggest subdividing frosting by chemical treatment into six groups depending on the method of depositing fluoric compounds on glass surface:

– frosting with paste;
– frosting in solution;
– frosting with hydrofluoric acid vapor;
– frosting by stamping inscription;
– pantographic and guillioshire frosting;
– frosting by dry compositions.

Paste frosting is used on glassware as an additional method for decorating household glassware, for instance, in combination with polishing. The main component of such

[1] Belgorod State Technological Academy of Construction Materials, Belgorod, Russia; Belgorod University of Consumer Cooperation, Belgorod, Russia.



Scheme 1. Technological scheme of frosting glass and glassware.

pastes is usually acid ammonium or potassium fluoride and also barium sulfate and dextrin as auxiliary components.

Frosting in solutions is used at factories producing lamp and sheet glass and household glassware. This method allows for control of the frosting process over a wide range and makes it possible to obtain such varieties as rough frosting, "frosty" dull finish, and fine and silky frosting [5]. Foreign producers, in particular in Czech Republic [6] are developing methods for intensification of the frosting process. The main components for frosting, as a rule, are ammonium or potassium fluorides in a solution of hydrofluoric acid [4, 5].

Frosting by the vapor of hydrofluoric acid in the presence of water vapor is used for dull finishing of sheet glass and other products [5]. Japanese researchers have recently proposed using such components as CCl_2F_2, $CHCl_3$, CCl_4, and $CFCl_3$ for frosting.

In frosting by stamping or inscription, a solution consisting of ammonium fluoride, hydrofluoric acid, and other components is applied to the glass surface by means of a pen, a brush, or a stamp [1, 5]. For simultaneous mass transposition and copying of patterns, which can be magnified or reduced, pantographs and grinding machines are used [2, 5].

On February 21, 2002 the All-Russia Conference of managers and designers of industrial enterprises of Russia took place in Moscow, where it was noted that among the most popular frosting methods are the "theme facet" and "Halle" methods together with polishing [7, 8]. Halle involves hydrofluoric acid etching of polychromic patterns deposited on superposed laminar glass [9].

Frosting by chemical treatment has a lot of valuable advantages and makes it possible to obtain unique artistic products; however, this is a toxic production. Therefore, an intense search for safer frosting methods is in progress [8, 9].

A dull surface can be obtained by depositing a fired coating imitating the etching effect onto the glass surface. The advantages of this method include elimination of energy-consuming machinery and toxic chemical compounds. The disadvantage consists in the fact that the surface of articles is not as smooth as in real etching. However, producers in the USA have recently obtained coatings whose quality is not inferior to those of chemical frosting [10].

Unfired coatings are becoming increasingly popular in our country and abroad. Unfired coating simulating the frosting effect are obtained by depositing white and semi-transparent inorganic varnishes and paints, as well as such polymers as polyurethane composites. Compared to other dulling methods, this one is less energy-consuming and not toxic [10].

The laser is an alternative energy source. It is successfully used for dull finish of glass articles [1]. A method using laser technology for decorating glassware (cups, vases, bottles, etc.) has been developed in Great Britain. A focused laser beam allows for making lines and single spots 30 – 100 nm in diameter on glass surface. Apart from the laser, ultrasonic treatment and etching by electric current are used for frosting glass articles [1, 2].

The Belgorod State Technical Academy of Construction Materials is currently researching frosting glass articles by detonation and plasma treatment (USSR Inventor's Certif. No. 1088265) [11 – 13]. A technology for dulling glass articles by plasma spraying of metal has been developed (Scheme 1). This is done using a UPU-8M electric plasma gun with a GN-5R plasma burner. The operational parameters of the plasma gun are as follows: work voltage 32 V, current strength 300 A. Argon is the plasma-forming gun with a flow rate of 2.5 m^3/h at a pressure of 0.25 MPa. The water consumed in chilling has a flow rate of 10 liters/min. The metal used for frosting is copper wire waste of diameter 1.0 – 2.5 mm.

Dull finish is implemented as follows. A melted metal drop brings sufficient heat to the point of contact with the glass substrate surface to soften the surface layer. As a consequence of the significant thermal shock, microcracks emerge in the surface layer at a depth of 200 – 250 nm and evolve to microchips. The deposited metal layer as a consequence of the thermal shock scales off the surface together with surface glass particles. A continuous field of microchips forms a high-quality dull surface of the "frosty" type.

Decoration was performed on products (wine and liqueur glasses) of the Krasnyi Mai Glass Works. Before decoration the glass surface was degreased with a cotton wool tampon impregnated in acetone or methanol. Then a stencil made of flexible aluminum or copper foil was applied to the surface. The article together with the stencil was inserted in a rotating tournette, and plasma spraying of copper was performed. Decoration of one piece lasted 10 – 30 sec depending on the

configuration and the surface area of the pattern deposited. After plasma treatment the stencil was removed and the glass surface was cleared of residual metal.

This method of frosting is less energy-consuming than such traditional methods as sandblasting and grinding with abrasive materials. The latter methods involve substantial dust contamination of the working zone and high energy consumption. Thus, the power of the respective electric plant can reach 20 kW or more, whereas the power of an electric-blowing plasma gun is 9 – 12 kW. The frosty dull surface produced by the traditional method has a conchoidal fracture and a medium depth of micropinholes up to 300 – 400 nm. Glass articles after plasma frosting have a similar surface with a conchoidal fracture. The depth of micropinholes after the deposited metal layer scales off is 300 – 350 nm.

The main advantages of frosting glass articles by plasma spraying include high output, environmental safety, and possibility of utilizing metallic wire waste. All this makes it possible to reduce production cost and to improve competitiveness of the product.

REFERENCES

1. O. L. Al'takh and P. D. Sarkisov, *Grinding and Polishing of Glass and Glass Articles* [in Russian], Vysshaya Shkola, Moscow (1988).
2. Yu. A. Guloyan, *Decorative Treatment of Glass and Glass Articles* [in Russian], Vysshaya Shkola, Moscow (1984).
3. Yu. A. Guloyan, *Technology of Glass Containers and Household Glass* [in Russian], Legpromizdat, Moscow (1986).
4. *Glass, Reference Book* [in Russian], Stroiizdat, Moscow (1973).
5. M. Vacek and V. Kupf, *Chemical Treatment of Glass* [Russian translation], Legkaya Industriya, Moscow (1974).
6. M. Maryska, "Corrosion of glass with stress in the water and acid solutions," in: *19th Int. Congr. on Glass* (2001), pp. 432 – 433.
7. A. V. Chukonova, "Specific features of the fashion glass school at the Gusevskii Crystal Works," *Steklo Mira*, No. 1, 69 – 72 (2002).
8. L. S. Matosyan, "Design and contemporary fashion glass," *Steklo Mira*, No. 1, 67 – 68 (2002).
9. S. A. Khvorostukhina, *Working with Glass* [in Russian], Veche, Moscow (2000).
10. I. D. Robertson, "Decoration of glass in the feeder channel," *Steklo Mira*, No. 1, 78 – 83 (2002).
11. V. S. Bessmertnyi, N. I. Min'ko, V. P. Krokhin, and A. A. Lyashko, "Decoration of glass and glassware by the plasma spray-deposition method," *Steklo Mira*, No. 3, 58 (2002).
12. V. S. Bessmertnyi, *Plasma Decorative Treatment of Wall Ceramics and Glassware, Author's Abstract of Candidate's Thesis* [in Russian], Riga (1987).
13. I. I. Nemets, V. P. Krokhin, V. S. Bessmertnyi, and A. I. Silko, "Plasma frosting of household glass," *Steklo Keram.*, No. 12, 8 – 9 (1983).